THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2008, *112,* 4405–4409
Published on Web 04/11/2008

Theoretical Elucidation of Conflicting Experimental Data on Vertical Ionization Potentials of Microhydrated Thymine

David M. Close*

Department of Physics, Box 70652, East Tennessee State University, Johnson City, Tennessee 37614

Carlos E. Crespo-Hernández

Department of Chemistry, 10900 Euclid Avenue, Case Western Reserve University, Cleveland, Ohio 44106

Leonid Gorb and Jerzy Leszczynski

Computational Center for Molecular Modeling Structure and Interactions, Department of Chemistry, Jackson State University, P.O. Box 17910, 1325 Lynch Street, Jackson, Mississippi 39217

Received: November 24, 2007; Revised Manuscript Received: February 6, 2008

In a recent article we reported calculations of the ionization energy thresholds (IET) of microhydrated thymine (Close; et al. *J. Phys. Chem. A*, **2006**, *110*, 7485). Calculations showed a distinct effect of microhydration on the IET's of thymine. The first water molecule was seen to decrease the IET by about 0.1 eV, and the second and third water molecules caused a further decrease of less than 0.1 eV each. These changes in IET calculated for the canonical form of thymine with 1−3 waters of hydration are smaller than the experimental values determined by Kim et al. (*J. Phys. Chem. C* **1996**, *100*, 7933). In the present study it has been shown that there is considerable reorientation of the water molecules in microhydrated thymine upon ionization. This leads to the expectation that the experimental ionization energies may therefore represent an adiabatic process. The results presented here show that the changes in experimental ionization energies determined by Kim et al. for microhydrated thymine are in good agreement with the calculated adiabatic ionization energies.

Introduction

In a recent article in this journal we reported quantum chemical calculations of the vertical ionization energy thresholds (VIET) of microhydrated thymine.[1] Calculations showed a distinct effect of microhydration on VIET's of thymine. The first water molecule was seen to decrease the VIET by about 0.1 eV, and the second and third water molecules caused a further decrease of less than 0.1 eV each. However, these changes in IET (ΔIET) calculated for the canonical form of thymine with 1−3 waters of hydration are smaller than the experimental values determined by Kim et al.[2]

Because there is a possibility that the experiments involve mixtures of different tautomeric forms, and calculations on the canonical form of thymine (diketo) did not fit the experimental data well, calculations on various microhydrated thymine enol−keto tautomers were also performed. A summary of these results was shown as Table 1 in Close et al.[1] and is included here as Supporting Information.

The results of this previous study showed that one can locate tautomers of microhydrated thymine whose calculated ΔVIET's do agree with the experimental data. However this agreement comes at considerable costs. The energies of these enol−keto tautomers are relatively high, >10 kcal/mol above the energy of the canonical form (diketo) of thymine. This means that if an ensemble of canonical thymine were in equilibrium (at room temperature), less than 1% of the molecules would be tautomerized. Thus, the conservative approach taken by others has been to state that the species observed under supersonic jet conditions should have only the most stable species.

TABLE 1: Experimental Data on the ΔIET's for Hydrated Thymine

T + nH_2O	ΔIET (eV) experimental[a]	ΔIET (eV) experimental[b]
thymine	9.15 ± 0.15	8.90 ± 0.05
Thy + $1H_2O$	8.85 ± 0.05	8.75 ± 0.05
Thy + $2H_2O$	8.65 ± 0.05	8.60 ± 0.10
Thy + $3H_2O$	8.50 ± 0.05	8.60 ± 0.10

[a] Ref 2. [b] Ref 5.

It is still necessary to explain the experimental results of Kim et al.[2] One can argue that information on how these products are created is not available from the cluster beam experiments. The jet-cooled experiments deal with the products observed downstream and are not able to access the upstream processes of formation. Certainly there is energy available to produce a variety of products, but one really needs to know which ones will actually be produced in sufficient quantity, and with sufficient long lifetimes, to permit detection.

These issues are currently unresolved. It is interesting, however, to note recently that there is some evidence reported

---

* To whom all correspondence should be addressed. E-mail: closed@etsu.edu.

10.1021/jp711157b CCC: $40.75

for the existence of several rare tautomers of guanine whose stabilities lie 3−7 kcal/mol above the canonical form of guanine in the gas phase.[4] However, given the relative energies of the thymine tautomers presented in our previous study,[1] it seems important to look for alternative answers to explain the ΔVIET results on microhydrated thymine reported by Kim et al.[2]

A new experimental paper has appeared that reports single photon ionization studies of the microhydratred DNA bases.[5] The new experiments and the results, however, are different from those previously reported by Kim et al.[2] Table 1 shows the IET values obtained for the microhydrated thymines in these two experiments.

The first thing one notes in Table 1 is the smaller ΔIET's in the new results. The real difference however comes in the author's interpretation of these results. The 8.90 eV IET of thymine reported by Belau et al.[5] is very close to the 8.9178 eV adiabatic ionization potential recently reported by Choi et al.[6] *The authors therefore state that these new results represent adiabatic appearance energies*. This is different from the assumptions made in interpreting the original experiments of Kim et al.[2] where the appearance energies were scaled to the vertical ionization potentials reported by Hush and Cheung.[7] Therefore, all of the calculations we have previously reported have been vertical ionization potentials.[1]

It is important to discuss the differences in the two sets of experimental results. The original experiments performed by Kim et al.[2] used electron impact ionization to measure the appearance energies of thymine and adenine complexed with water. In their cluster-beam experiments, the ionization energy of thymine was not actually determined. The experimental data were scaled to match the experimental IET's reported by Hush and Cheung.[7] Thus, whether or not these experiments involved vertical or adiabatic ionizations could not be determined.

The new experiments by Belau et al. also share this uncertainty.[5] The authors did not actually determine whether or not their experiments involved vertical or adiabatic ionizations. In these new experiments, however, the authors did actually measure the ionization energy thresholds. They report that their results represent adiabatic appearance energies based on the very close agreement of the measured ionization energy of thymine to the adiabatic ionization potential in the literature.

It is also important to comment on the accuracy of the experimental measurements. The electron impact ionization data show a very flat increase above the threshold so Kim et al.[2] report the "estimated absolute accuracy of their ionization potentials is ±0.15 eV, but the relative values are perhaps 3-fold better". The experimental results reported by Belau et al.[5] involve a different set of problems in determining the ionization energy. From the photoionization efficiency (PIE) curves, the authors show there are obvious signal-to-noise problems with estimating the appearance energies reported. The authors note that their procedures for determining the appearance energies work best when there are relatively good Franck−Condon factors in the ionization process. This point will be discussed in more detail below.

So the two sets of data presented in Table 1 represent two different experimental techniques and interpretations of the results. The first set of data (Kim et al.[2]) are scaled to vertical ionization potentials, and the second set (Belau et al.[5]) are said to represent adiabatic ionization potentials. *It is the purpose of the present contribution to compare theoretical vertical ionization potentials previously reported with new calculations of adiabatic ionization potentials of microhydrated thymine in efforts to ascertain if the reported experimental results by Kim et al.[2] more likely represent vertical or adiabatic ionization potentials.*

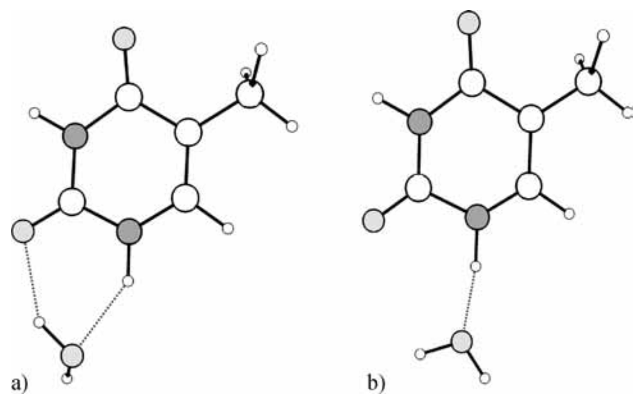

Figure 1. (a) Neutral Thy1. (b) Optimized one electron oxidized Thy1.

Computational Methods

Previous calculations on microhydrated thymine involved taking the best geometries available in the literature for thymine with various waters of hydration as input parameters, and optimizing the structures at both the B3LYP/6-31++G(d,p) and P3/6-31++G(d,p) levels of theory.[8] Calculations to obtain vertical ionization energies were performed at the B3LYP level, and electron propagator calculations in the partial third-order (P3) approximation levels of theory using the standard 6-31++G(d,p) basis set. B3LYP harmonic vibrational frequency calculations were performed with the same basis set to verify the nature of the PES stationary points. Calculations were performed on the Gaussian 98 suite of programs.[9] Although the electron propagator methods have been shown to be very reliable in calculating vertical ionization energies, they are not currently configured to calculate adiabatic ionization energies.

Vertical ionization energy calculations involve evaluation of the difference in total energy between the cation radical and the neutral base in the geometry of the neutral species (optimizations of the neutral molecule using the 6-31++G(d,p) basis set followed by a single point calculation on the cation at the same level of theory). Adiabatic ionization energies involve an optimization of the cation. These optimizations can be very time-consuming. To save computer time, the optimized geometries of hydrated thymine were determined at the B3LYP/6-31+G(d) level of theory, and then the cation was optimized at the same level of theory. A table in the Supporting Information shows that the same level of accuracy in determining adiabatic IET's (AIET) is obtained with 6-31+G(d) as with the previous 6-31++G(d,p) level of calculations. Therefore, the various adiabatic ionization potentials calculated herein were computed using the more efficient 6-31+G(d) basis set level of theory.

Figure 1 shows the changes Thy1 undergoes upon ionization. One sees that for the neutral form of Thy1, the water participates as both a hydrogen-bond donor and acceptor, in the N1−H, C2=O region. However, in the cationic form of Thy1, the water acts only as a hydrogen bond acceptor in the N1−H region and has moved a considerable distance away from the C2=O.

For the present discussion it is convenient to use the same labeling scheme as used previously.[3] It is interesting to note that there are fewer optimized cation structures than previously identified in doing the vertical IET calculations. For example, in the previous study there were distinct Thy2 and Thy3 neutral

TABLE 2: Adiabatic Ionization Potential Calculations Compared with Experimental Data

	IET (eV) experimental Kim et al.	ΔIET (eV)	IET (eV) experimental Belau et al.	ΔIET (eV)	adiabatic IET 6-31+G(d) (eV)	ΔAIET (eV)
thymine	9.15 (8.92)[a]		8.90		8.78	
Thy1*	8.85 (8.62)	0.30	8.75	0.15	8.45	0.33
Thy2					8.51	0.27
Thy3					8.53	0.25
Thy11*	8.65 (8.42)	0.20	8.60	0.15	8.40	0.05
Thy12					8.21	0.24
Thy13					8.25	0.20
Thy33					8.54	0.00
Thy111*	8.50 (8.27)	0.15	8.60	0.00	8.32	0.08
Thy113					8.23	0.17
Thy133					8.26	0.14

[a] The microhydrated thymines marked with an asterisk have the lowest energy in each set. Numbers in parentheses are scaled to the adiabatic ionization potential of Thy.

structures. If one tries to optimize the Thy2 cation, the water ends up in the same position as the Thy3 cation, directly in front of the N3−H proton (analogous to the cation of Thy1 shown above).

Results and Discussion

Table 2 shows the new adiabatic ionization potential calculations on microhydrated thymine (column 6). For easy comparisons the ΔIET's of Kim et al.[2] and Belau et al.[5] have been included here. One sees that the ΔAIET calculations in column 7 agree best with the results of Kim et al. (third column). Because Kim et al.[2] scaled their data to represent vertical ionization potentials, the IET's are higher than the calculated IET's shown in the sixth column. If the data presented by Kim et al.[2] are instead scaled to the adiabatic ionization energy of 8.92 eV (shown here in parentheses in column 2), then one sees a remarkable agreement between experimental and calculated ΔIET results (columns 3 and 7).

For the thymine dihydrates in Table 2, Thy11 does have the lowest energy. However, Thy13 differs in energy by only ca. 3 kcal/mol. So, although the ΔAIET between Thy1 and Thy11 does not compare well with the experimental ΔAIET, it is likely that the experimental value represents a sampling of ionization energies from several low lying thymine dihydrates. For the thymine trihydrates Thy111 has the lowest energy, but Thy113 is higher in energy by only 0.55 kcal/mol. So the ΔAIET between Thy113 and Thy11 is 0.17 eV, in better agreement with the experimental results.

As seen in Table 2, the agreement of the calculated adiabatic ionization potentials with the new experiments of Belau et al.[5] is not quite as good as for those of Kim et al.[2] The problem is that the experimental ΔAIET's (column 5) are smaller than the computed ΔAIET's (column 7). This may have to do with problems in estimating the onset value for the appearance energy of thymine or with stability problems of the thymine cation. Looking at the author's PIE curves (the author's Figure 3) one sees that a straight line through all the data could give a slightly higher appearance energy for thymine.[5] Also, for the thymine $+ 3H_2O$ PIE curve it looks as if a slightly smaller appearance energy would also fit the data shown, given the large error bars.

There are several types of experiments used to determine ionization potentials given in Table 3. The first entries in Table 3 are reported from photoelectron spectroscopy (PES) experiments and provide vertical ionization energies. One notes the rather good agreement from three experiments with results of approximately 9.18 eV.

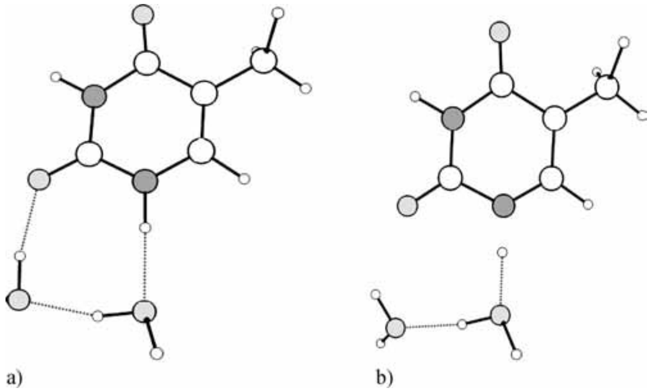

Figure 2. (a) Neutral Thy11. (b) Optimized one electron oxidized Thy11.

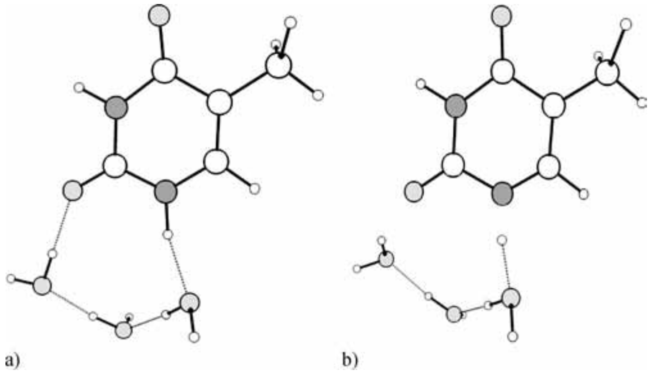

Figure 3. (a) Neutral Thy111. (b) Optimized one electron oxidized Thy111.

Photoionization mass spectroscopic (PIMS) experiments are used to determine adiabatic ionization potentials. In Table 3 one can see that the two PIMS experiments report ionization energies below 8.90 eV. For the present discussion it is important to note that there is only a small difference of ca. 0.3 eV between the PES and PIMS experiments.

There is also a new high resolution VUV ionization spectroscopic experiment performed by Choi et al.[6] This experiment is labeled MATI (for mass-analyzed threshold spectroscopy) in Table 3. The MATI value is 8.9178 ± 0.001 eV for the adiabatic ionization potential of thymine. This value is only 0.1 eV higher that the PIMS values in Table 3.

Next we must look at the experiments already considered by Belau et al.[5] They describe single photon UV photoionization studies (VUV SPI) of microhydrated thymine. The appearance

TABLE 3: Experimental Determination of Thymine Ionization Potentials

method	ionization potential	reference
PES	9.14 ± 0.03	Hush et al.[7]
PES	9.18	Urano et al.[10]
PES	9.19	Trofimov et al.[11]
PIMS	8.87 ± 0.05	Orlov et al.[12]
PIMS	8.82 ± 0.03	Jochims et al.[13]
VUV MATI	8.9178 ± 0.001	Choi et al.[6]
VUV SPI	8.90 ± 0.05	Belau et al.[5]

energy for thymine is determined to be 8.90 ± 0.05 eV. This value is close to the VUV MATI experimental results of Choi and co-workers.[6] One sees that in Table 3 the results of Belau et al.[5] are slightly higher than those of Jochims and co-workers.[13] Belau et al. mention that the values quoted by Jochims could be explained by insufficient cooling in the evaporation source leading to a lower ionization onset due to hot band effects.[5] With the accuracy quoted, it seems safe to say that the appearance energies determined by Belau et al.[5] are adiabatic ionization energies.

The original experiments performed by Kim et al.[2] involve electron impact (EI) and are typically considered to involve a vertical process. Therefore one expects the ionization energies to agree with the results of the PES experiments reported in Table 3. But this statement has to be qualified. The electron impact technique can yield ionization energies that are reliable to within 0.10 eV. We have already noted that in their work, Kim et al.[2] report conservative absolute accuracy of ±0.15 eV. On the other hand, the ionization values determined by PES studies are generally accurate to 0.01−0.02 eV.

Most of the experimental results shown in Table 3 involve only thymine in the gas phase. For the present study it is important to concentrate on the two studies that actually involve microhydrated thymine in the gas phase. In these two studies there seems to be fundamental limitation in both the EI experiments of Kim et al.[2] and the newer VUV SPI results of Belau et al.[5] The experimental photoionization curves of hydrated thymine in both experiments are characterized by a slow rise of the photoionization current at onset. This characteristic has been interpreted as a signature of a geometry change between the neutral and the ionic complex. In these cases, the Franck−Condon principle forbids the transition from the neutral ground-state to the cation ground state. Ionization can only occur when the photon energy is high enough to reach an excited vibrational intermediate state of the cation which allows the cation complex to explore conformations that might be similar to those of the neutral ground state.

It is therefore important to consider the geometry changes thymine (and microhydrated thymine) undergoes upon one electron loss. Improta et al. have previously looked at the calculated structural parameters of neutral thymine and of the radical cation of thymine.[14] They see no loss of planarity upon ionization of thymine. The important changes reflect bond length and bond angle changes in the C2−N1−C6-C5 region of the molecule. For the present study, it is important to ask if the waters of hydration alter this pattern. The results are presented in Table 4. Although there are significant shifts in the position of the water molecule as shown in Figure 1, the changes in the structural parameters between the neutral form and the cationic form of Thy1 are very similar to those noted by Improta et al.[14]

It is interesting to note the entries in Table 4 marked with an asterisk. These are the most prominent bond length changes in the pyrimidine ring. Inspection of the frequency calculations shows ring breathing modes in the neutral Thy1 complex (number 28 at 1241 cm^{-1} and number 30 at 1387 cm^{-1}) that involve simultaneous N1−C2 stretching, N1−C6 contraction, and C6−C5 stretching. Also of interest is the most intense band at 3422.2 cm^{-1} that corresponds to N1−H stretching. This band shifts to 2975.3 cm^{-1} in the cation. The pK_a of the thymine radical cation is 3.6.[15] Thus, this intense band represents the pathway for deprotonation of the radical cation to form a hydronium ion and the neutral thymine radical.

TABLE 4: Geometry Changes of Thy1 Monohydrate upon Oxidation

bond length	Thy1 neutral	Thy1 cation
N1−C2	1.3788	1.4369*
N1−C6	1.3785	1.3233*
C2−N3	1.3790	1.3748
N3−C4	1.4102	1.4014
C4−C5	1.4654	1.4900*
C5−C6	1.3558	1.4109*
C5−C7	1.5022	1.4768
C2−O8	1.2337	1.2070
C4−N4	1.2248	1.2136
N1−Ow	2.8200	1.2170
O8−OwH1	1.9265	3.0560

There is a similar influence of the water molecules exhibited by the thymine + 2H_2O structures. Figure 2 shows the neutral Thy11 dimer before and after one electron oxidation. As with the Thy1 example above, the water moves away from the C2=O. In the neutral Thy11 the C2=O···H distance is 1.797 Å. This distance increases to 2.381 Å in the cation. The second water molecule in the dimer acts as a proton acceptor. The N1−H distance is 1.034 Å in the neutral Thy11, but increases to 1.090 Å in the cation. A vibrational frequency calculation shows that the most intense transition again is associated with N1−H stretching. This transition is 3238.9 cm^{-1} in the neutral Thy11 and shifts downward to 2381.1 cm^{-1} in the cation.

The results of calculations in Table 2 show that the lowest energy configuration for thymine + 3H_2O is for Thy111. The shift in position of the waters in Thy111 upon oxidation is shown in Figure 3. In the neutral Thy111 the distance from the C2=O to the hydrogen on the first water molecule is 1.7788 Å. This distance shifts to 2.1259 Å in the cation. The N1−H distance is 1.0338 Å in the neutral Thy111, and shift to 1.1053 Å in the cation. The most intense vibrational band is again associated with N1−H stretching. This band is 3235.8 cm^{-1} in the neutral Thy111 and shifts downward to 2169.3 cm^{-1} in the cation.

So it is clear that there are significant geometry changes in the three microhydrated thymines considered here before and after one electron removal. It is now useful to consider if such geometry changes have an influence on the ionization potentials.

An important paper by Hildenbrand[16] compares experimental ionizations energies derived from electron impact (EI) studies and from photoelectron spectroscopy (PES). It is reported that in PES spectra for which there is no change in the molecular geometry during ionization, the initial peak in the lowest energy band is the most intense, indicating that the vertical and adiabatic thresholds are coincident. However, in polyatomic molecules the impact energy may be distributed over a large number of internal modes. Because the EI ionization is considered to be a vertical process by the Franck−Condon principle, one expects that the EI ionization energies would be more in accord with the PES ionization energies. *A surprising result of this EI/PES comparison is the correlation of the EI threshold ionization energies in polyatomic molecules with the adiabatic ionization energies determined by PES rather than with the vertical ionization energy values.*

An example given by Hildenbrand[16] concerns ionization of CF_2 where the adiabatic and vertical ionization energies differ by 0.82 eV. The accurate photoionization threshold value for CF_2 is 11.445 ± 0.025 eV, which is in close agreement with the PES adiabatic ionization energy. Calculations at the level presented here show the vertical ionization energy to be 12.33 eV and the adiabatic ionization energy is 11.46 eV. In the neutral molecule the F−C−F angle is 104.24° but increases to 124.34° in the cation. This leads Hildenbrand to the conclusion that *where molecular geometry changes lead to significant differences between adiabatic and vertical ionization energies, the EI values unexpectedly tend to agree with the adiabatic rather than the vertical ionization energies*.[16]

In our previous study on microhydrated thymine[1] it was shown that the changes in ΔIET calculated for the canonical form of thymine with 1−3 waters of hydration are smaller than the experimental values determined by Kim et al.[2] The previous study showed that one can locate enol−keto tautomers of microhydrated thymine whose calculated ΔIET's do agree with the experimental data.[1] However, this is an unlikely explanation of the data because there is no experimental evidence that thymine has any low lying tautomers. This conclusion therefore led to the need for the present, more comprehensive study.

It has also been shown that the adiabatic ionization potential calculations on microhydrated thymine presented here do not agree as well with the new VUV SPI results of Belau et al.[5] This seems to be due in part to uncertainties in determining where the actual thresholds are in the experimental data, and the poor signal-to-noise ratio for their TW_2 and the TW_3 measurements. But there are also difficulties in comparing the results of two different types of experiments (electron impact versus photoionization). There is of course no way of knowing if both experiments are actually accessing the same ionization state. It is interesting to note that in the paper by Belau et al.[5] there are also data on the ionization energies of the other DNA bases. Our efforts are now directed at understanding and elucidating these results.

Conclusions

There is disagreement in the literature among different experimental determinations of the vertical ionization potentials of microhydrated thymine. The results of calculations presented herein indicate that the original EI experimental results reported by Kim et al.[2] most likely represent adiabatic appearance energies and not vertical ionization potentials.

Because electron impact experiments such as those performed by Kim et al.[2] are considered to represent a vertical process in the spirit of the Franck−Condon principle, it is expected that the measured ionization energies would be in accord with the vertical ionization energies measured in PES experiments. Indeed this is why Kim et al.[2] scaled their measurements to the vertical ionization energy of thymine as determined by Hush and Cheung.[7] However, electron impact studies only yield vertical ionization energies when there is little or no change in molecular geometry during ionization.[16]

In the present study it has been shown that there is considerable reorientation of the water molecules in microhydrated thymine upon ionization. This therefore leads to the expectation that the experimental ionization energies reported by Kim et al.[2] may therefore represent an adiabatic process. The results presented here show that the changes in experimental ionization energies determined by Kim et al.[2] for microhydrated thymine are in good agreement with the calculated adiabatic ionization energies.

Supporting Information Available: Energy values for the thymine tautomers and monohydrates. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Close, D. M.; Crespo-Hernández, C. E.; Gorb, L.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 7485–7490.

(2) Kim, S. K.; Lee, W.; Herschbach, D. R. *J. Phys. Chem.* **1996**, *100*, 7933–7937.

(3) The notation here follows the notation in paper IV in this series (ref 1 herein).

(4) Mons, M.; Piuzzi, F.; Dimicoli, I.; Gorb, L.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 10921–10924.

(5) Belau, L.; Wilson, K. R.; Leone, S. R.; Ahmed, M. *J. Phys. Chem. A* **2007**, *111*, 7562–7568.

(6) Choi, K.-W.; Lee, J.-H.; Kim, S. K. *J. Am. Chem. Soc.* **2005**, *127*, 15674–15675.

(7) Hush, N. S.; Cheung, S. A. *Chem. Phys. Lett.* **1975**, *24*, 11–13.

(8) Dolgounitcheva, O.; Zakrzewski, V. G.; Ortiz, J. V. *Int. J. Quantum Chem.* **2002**, *90*, 1547–1554.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian: Pittsburgh, PA, 1998.

(10) Urano, S.; Yang, X.; LeBreton, P. *J. Mol. Struct.* **1898**, *214*, 315–328.

(11) Trofimov, A. B.; Schirmer, J.; Kobychev, V. B.; Potts, A. W.; Holland, D. M. P.; Karlsson, L. *J. Phys. B* **2006**, *39*, 305–329.

(12) Orlov, V. M.; Smirnov, A. N.; Varshavsky, Y. M. *Tetrahedron Lett.* **1976**, *48*, 4377–4378.

(13) Jochims, H.-W.; Schwell, M.; Baumgartel, H. L. S. *Chem. Phys.* **2005**, *314*, 263–282.

(14) Improta, R.; Scalmani, G.; Barone, V. *Int. J. Mass Spectrom.* **2000**, *201*, 321.

(15) Steenken, S. *Free Radical Res. Commun.* **1992**, *16*, 349–379.

(16) Hildenbrand, D. L. *Int. J. Mass Spectrom.* **2000**, *197*, 237–242.

JP711157B